ELECTROLESS COPPER PLATING OF ELECTRONIC DEVICE COMPONENTS

FIELD OF THE INVENTION

This invention relates to the manufacture of metal components, such as lines, vias, and trenches, utilized in the production of semiconductor devices and Printed Circuit Boards (PCBs), and more particularly, to an improved method and composition for applying electroless copper.

BACKGROUND OF THE INVENTION

US Pat. 2002/0011416 A1 (Landau), US Pat. 6319831 (Tsai) and US Pat. 6180523 (Lee) are indicative of the prior art.

Copper has increasingly gained prominence as the preferred metal in prior art interconnect technology, due to its low cost and superior conductivity. Hence, the recent technological focus in the semiconductor devices and Printed Circuit Boards production industries on developing manufacturing techniques and compositions to improve the current state-of -the art for applying electroless copper plating.

Today, the reduction or deposition of copper metal from solution, is performed either by electrolytic or electroless plating. Currently, the industry favors electrolytic plating (electroplating) over electroless plating. To understand this preferrence, consider some of the salient advantages and disadvantages of each process, as listed below:

- **Advantages of electroplating:**
  1. Relatively low production cost per unit weight of plated copper, since the reduction process of Cu^{++} to Cu^{0} (copper metal) is performed using low cost electrical current.
  2. Electrolytic reduction deposits high quality metal.
  3. Higher rate of deposition, typically 20-25 micron films achievable in one hour or less, enabling higher throughput.
  4. Lower waste generation rate.
- **Disadvantages of electroplating:**
  1. High capital investment and equipment maintenance cost.

2. Stringent process window.
3. Limited deposit-application capability, resulting in a lack of uniformity in the deposited copper film thickness. Especially problematic, in view of the increasing trend towards plating high aspect-ratio geometries, of vias, microvias, trenches and other metal components.

- **Advantages of electroless plating:**
  1. Low capital investment and control instrumentation cost.
  2. Low equipment maintenance and installation cost.
  3. Excellent thickness uniformity of plated Cu film. This feature is of special significance when plating high aspect-ratio geometries.
- **Disadvantages of electroless plating:**
  1. Lower rate of deposition, typically 20 hours or more, to deposit a 20-25 micron film, resulting in low production throughput.
  2. Higher plating cost per unit weight of plated copper, due to the use of additional chemicals, as opposed to inexpensive electrochemical reduction that uses electrical current.
  3. Inferior plate quality that can result in functional device failure, as for example, when the components are subjected to thermal stress.
  4. Low copper-to-substrate adhesion.
  5. Greater waste generation rate than in electroplating.

The most attractive feature of electroless plating is its inherent deposited plate thickness uniformity. Its most problematic attributes are its low rate of deposition and its inferior functional plate quality. If the aforementioned problematic attributes were minimized or eliminated, electroless plating would most probably supplant electroplating as the preferred plating process for the production of semiconductor devices and Printed Circuit Boards.

SUMMARY OF THE INVENTION

Accordingly, it is a principal object of the present invention to overcome the above-mentioned problems and provide an improved method and composition for applying electroless copper, that will enable electroless copper plating to become a preferred alternative to electroplating, for the fabrication of electronic devices.

The present invention provides a method and composition that improve the deposition plating rate of electroless copper. To achieve this, the invention presents embodiments comprising using elevated plating temperatures, coupled with suitably designed bath compositions, to preserve the electroless bath stability, required to improve the deposition plating rate of electroless copper.

The present invention also provides a method and composition that improves the quality of electroless copper coatings or films, without lowering the rate of deposition, by combining elevated interfacial substrate or solution temperatures with suitably engineered solution chemistry. In one embodiment the electroless bath composition comprises suitable individual Cu^{++} and Cu^{+} complexing agent(s), or a combination of complexing agents, surfactants, organic polymer additives, and the like, many of which can be adapted from the prior art, and suitably optimized. For example, potential organic additive types or surfactants can be Polyoxes; Pluronics; Polyols; Polyglycols; Carbowaxes; Hydroxy ethyl cellulose (HEC), carboxy acetylenic, or fluocarbon acetylenic surfactants.

The method and composition of the present invention enable the production of electroless copper coatings with improved adhesion to the substrate. This is achieved by selecting activation systems that result in copper initiation at moderate rates. An electroless copper composition assists, in that it too, ensures slow initial copper reduction at the substrate-solution interface.

In some instances it may be beneficial to expose the surface to be plated to an electroless copper composition especially designed for slow "take-off " of the initial copper layer. This composition may differ from the electroless copper composition, designed to give the desired copper thickness.

In many instances it may be advisable to deposit an initial film, immediately

adjacent to the substrate-to be-plated, prior to plating electroless copper. This initial film deposit helps achieve improved adhesion, but more importantly, helps reduce copper migration. Potential candidates for "non-copper" films are electroless nickel, cobalt, gold, and alloys of copper or nickel. US Pat. 4482596 to Gulla, discloses one such method and composition that plates electroless nickel or copper coatings. Others can be found in the prior art literature.

The initial metal films can be very thin, often no more than a few Angstroms thick, optimizable through routine experimentation

The method of the invention affords electroless plating on non-conducting substrates without the use of precious metal sensitization. Examples of similar methods and compositions are disclosed in Israeli pending applications # 150364, 150577 and 150940.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

The present invention provides a method and composition that improve the deposition plating rate of electroless copper. The invention presents embodiments comprising using elevated plating temperatures at the substrate - solution interface. This is coupled with suitably designed bath compositions, to preserve the electroless bath stability, required to improve the deposition plating rate of electroless copper. Elevated plating temperatures can be attained by heating the electroless copper plating bath, by heating the substrate to the desired temperature (exemplified to some extent in US Pat. 2002/0086102), or by a combination of the two approaches.

When choosing to heat the substrate, it is recommended to dispense the electroless plating solution onto the substrate by using spraying or splashing techniques. In the latter case, the electroless plating solution should be stored in a storage vessel and recirculated, as is done in well-known processes involving photoresist developing solutions. A technique known as puddle development is used. This embodiment offers several advantages, some of which are listed below:

- Avoiding excessively high temperature electroless baths that may lead to their decomposition.
- The wafer to be plated can be spun during deposition. This is similar to techniques widely practiced in wafer lithography, which result in interfacial solution movement, contributing to improved adhesion and plate quality.

- The wafer can be heated selectively using thermal laser treatment, resulting in selective plating, as a potential means of achieving a desired copper pattern.
- Interfacial substrate-solution plating temperatures can be well over the boiling temperature of the electroless composition.

The above embodiment, wherein the substrate to be metallized, i.e.the wafer, is kept "hot", via contact with a heat source, or via radiant heat such as IR, thermal laser, microwave, and induction current, during electroless plating, coupled with "accommodating", tailor-made electroless copper chemistries, offers new possibilities for process improvements to those skilled in the art of electroless plating.

A preferred composition disclosed by the present invention comprises the following:

- A complexor or a combination of complexors, that afford superior bath stability at elevated temperatures. They will not form an overly "tight" or strong complex that would negatively impact the rate of copper deposition. For example, EDTA strongly complexes cupric copper, but it tends to diminish the rate of deposition. On the other hand, Rochelle salt tends to give high plating speeds, but fragile electroless solution stability. An optional embodiment of this patent comprises therefore, a blend of complexors, to balance bath stability and. rate considerations.

In choosing the desired complexor blend, one can be guided by the stability constant of copper complexors listed in appropriate handbooks.

- High reducer or copper ratios, again to favor rate.
- Stabilizers, monovalent copper (Cu+) complexors. Generally, these are other than thio derivatives and the like, which tend to result in stressed deposits, and can negatively impact Cu film quality. Desirable additives will comprise derivatives of pyridine (i.e. bipyridine), cyanides (i.e. alkali metal cyanides), cyanates, heavy metal cyanide complexes (i.e. ferrocyanides), and the like, many of which can found in the prior art literature and optimized through trial-and error experimentation.

It was discovered that electroless copper compositions of this invention can advantageously contain relatively high concentrations of stabilizing additives, such as bipyridine, significantly above levels or concentrations disclosed in the prior art. The reason perhaps lies in combining elevated operating temperatures with suitable electroless bath compositions, as suggested in this invention.

The embodiment of the present invention that focuses on improving plate quality will comprise:

- Annealing of the as-plated deposit, to relieve stresses. In choosing suitable annealing time or temperature conditions, one needs to guard against "overheating", that may lead to degradation of the workpiece, as for example, glass or epoxy laminates of PCBs. In the case of silica wafers, "overheating" is not an issue. They are known to undergo very high temperature processes without causing major defects. Although the risk of copper migration exists, the present invention minimizes it.

The capabilities of the present invention are further illustrated in the following examples:

Notes:

1. The sign (*) denotes, throughout this disclosure, products supplied in Israel by MacDermid Israed Ltd. and used in accordance to supplier's instructions.
2. The sample was exposed to the above process steps by immersion.
3. Following each process step, the sample was rinsed with water.

EXAMPLE 1

A 3"x3" copper -clad glass-epoxy pane, from which the copper has been etched away, was processed according to the following procedure:

a. Metex Conditioner 90 *

b. Water rinse.

c. Metex G-3 *

d. Mactivate 10 *

e. Metex 9071 *

f. Aqueous solution of Na_3PO_4, 5 min., RT.

g. Immerse for 2 hours, 70 deg.C, with intermittent work agitation in the following electroless copper solution, hereinafter referred to as "Micro-Via" composition.

Component	Concentration
$CuSO_4 . 5 H_2O$	15g/l
EDTA	25g/l
Quadrol	6g/l
Formaldehyde 37%	33g/l

Compon nt	Concentration
NaOH	13g/l
Bipyridine	100 ppm
NaCN	18 ppm
Petro Ag	10 ppm

h. Water rinse

i. Dry

Upon examination, the sample displayed a pink copper coating, with good adhesion (no apparent blisters or lifting of the deposit). Coating thickness was measured to be 8 microns thick.

EXAMPLE 2

Same as EXAMPLE 1, except:

- Prior to being immersed in the Micro-Via composition, the sample was immersed for 5 min. in a working solution of 9072*, then transferred without a water rinse to the Micro-Via composition.
- After two hours in the Micro-Via, the sample was water-rinsed and dried. The copper coating showed blistering or lifting from the substrate. Coating thickness was about 8 microns.

EXAMPLE 3

Same process steps as in EXAMPLE 1, except:

- The sample was made of double-sided copper-epoxy, containing interconnecting holes.
- Prior to step a, the sample was contacted with Metex 9221-S *, Metex 9275 *, and Metex G-3 *. Water rinsing following each process step.
- Plating time in the Micro-Via was approximately 6-7 hours, with 2-ml. formaldehyde added every 2 hours to one liter of Micro-Via.

After rinsing with water and drying, copper thickness in the holes was approximately 20 microns. After baking for approximately 24 hours in an air-circulating oven at approximately 150 deg C, no lifting of the plate from the substrate was observed. It was then exposed to the industry-accepted solder shock test. Metallurgical examination of the holes showed reasonable copper plate integrity and adhesion.

EXAMPLE 4

Same as EXAMPLE 1, except:

- Formaldehyde was increased by 10g/l.
- 50 g/l sodium carbonate was added and dissolved

After plating for 1 hour, no lifting of the deposit was observed, and thickness was determined as 3 microns.

EXAMPLE 5

Same as EXAMPLE 4, except:

- Sodium carbonate was increased to 100 g/l.

After plating for one hour, thickness was measured at 4.5 micron, and the copper coating showed some lifting.

EXAMPLE 6

A Pyrex glass plate was processed as in EXAMPLE 1, except:

- After Mactivate 10 * it was heated on a hot plate to a temperature estimated at over 200 deg. C.
- Then about 100 cc of Macudep 22 * solution (made up with 20 % of Macudep * concentrate A, 20 % concentrate B, and the balance DI water) was dispensed onto it.

After about 5 sec., a copious pink-colored copper layer covered the Pyrex plate.

Having described the invention with regard to certain specific embodiments, it is to be understood that the description is not meant as a limitation since further modifications may now suggest themselves to those skilled in the art, and it is intended to cover such modifications, as fall within the scope of the appended claims, namely combining elevated substrate temperature with suitably optimized electroless solution chemistry.

Also, while the invention has been described in terms of electroless copper, it encompasses other electroless metal depositions, such as electroless nickel, cobalt, alloys of nickel or copper, and the like.